

## PATENT ABSTRACTS OF JAPAN

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(54) BATTERY JAR FOR SEALED SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve gas barrier property by forming a vinylidene chloride resin layer in a battery jar for sealed secondary battery.

SOLUTION: A battery jar for sealed secondary battery formed of an alloy resin of polypropylene/polyphenylene ether resin having a polypropylene resin as matrix phase, a polyphenylene ether resin as dispersing phase, and a hydrogenated styrene-butadiene copolymer as compatible agent is covered with a vinylidene chloride resin having a molecular weight of 10,000-1,000,000 and vinylidene chloride content of 51-99wt. %.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the member suitable for manufacturing various rechargeable batteries, such as a lead accumulator and an alkaline cell. Furthermore, it is related with the battery case for sealing form rechargeable batteries which is excellent in warm water-proof permeability, gas-proof permeability, and chemical resistance in detail.

[0002]

[Description of the Prior Art] The application of various rechargeable batteries is being expanded from the power source for the data backup of a migration machine dexterous driving source and a computer and the purpose of a deployment of solar-battery energy, and a viewpoint of environmental protection. Although it is common knowledge that many rechargeable batteries are used in order to supply the required power of the internal combustion engine of an automobile especially, development of the so-called electric vehicle which makes the rechargeable battery itself a driving source instead of an internal combustion engine is also performed further briskly in recent years.

[0003] With development of an industrial technique, the need of a rechargeable battery tends to increase increasingly and the request to the rechargeable battery of small lightweight and large electric capacity is increasing.

[0004] Such a rechargeable battery has the indispensable battery case which contains an acid, or the electrolyte and electrode of alkali. The shock resistance which can also bear enough the resistance (it is gasoline-proof nature and oilproof further when used as a rechargeable battery of an automotive application) over strong acid and alkali, and an external impact as a property required of this battery case is required.

[0005] Furthermore, if this battery case is not what took into consideration enough hydrogen gas, generation of heat accompanying a chemical reaction, and a product, for example, moisture, etc. at the time of charge, it will not become.

[0006] If a sealing form rechargeable battery is hit, in order to make the request of lightweight[ small / ]-izing suit especially, in a battery case, it is thin meat, and there is thermal resistance, it is equal to the rise of the internal pressure at the time of charge, and it necessary to be able to maintain electrolytic description proper over a long period of time.

[0007] Many polypropylene resin and ABS plastics are conventionally adopted as an ingredient of a battery case. However, it is pointed out that is [ polypropylene resin ] comparatively large although polypropylene resin is excellent in steam barrier nature, and it is not enough as engine performance of a battery case. [ of the gas permeability of hydrogen and oxygen ] Moreover, although excelled in a moldability, in injection molding of the product of light-gage rib structure, troubles, like being surface discontinuity, such as HIKE produced since molding shrinkage is large, being rigidity, and it is inferior to especially the rigidity at the time of an elevated temperature (at the time of heat rigidity) are also pointed out. On the other hand, the point that ABS plastics are inferior in gas barrier nature, such as steam barrier nature and hydrogen, compared with polypropylene resin, and the point that it is inferior to

the resistance over a gasoline and oil (for example, brake oil, a rust-proofer) in an automotive application are pointed out.

[0008] Moreover, although the battery case for sealing form rechargeable batteries which consists of polyphenylene-ether system resin currently indicated by JP,6-203814,A and polystyrene system resin is excellent in steam barrier nature compared with ABS plastics, since the battery case fabricated with this resin constituent has the bad fluidity, in case heat welding of shaping distortion and the lid generated at the time of shaping carries out, in the problem and the object for automobiles which a stress crack generates by the thermal strain, the resistance over a gasoline and oil is pointed out like ABS plastics.

[0009] Thus, the rechargeable battery using the battery case manufactured with the conventional ingredient has the problem respectively, and was not able to obtain the battery case for sealing form rechargeable batteries which satisfies both steam barrier nature and the gas barrier nature of hydrogen and oxygen especially.

[0010]

[Problem(s) to be Solved by the Invention] This invention cancels the fault of the conventional technique and aims at offering the battery case for sealing form rechargeable batteries excellent in the gas barrier nature to the gas which occurs within steam barrier nature and a cell, such as hydrogen and oxygen, which can maintain the description of an early electrolyte over a long period of time.

[0011]

[Means for Solving the Problem] In order that this invention persons may solve said technical problem, as a result of repeating examination wholeheartedly, the battery case which has a vinylidene-chloride system resin layer finds out excelling not only in a steam but in gas barrier nature, such as hydrogen and oxygen, and came to make this invention.

[0012] That is, this invention relates to the battery case for sealing form rechargeable batteries excellent in the gas barrier nature characterized by having a vinylidene-chloride system resin layer.

[0013]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[0014] The vinylidene-chloride system resin as used in the field of this invention means the homopolymer of a vinylidene chloride, or the copolymer of a vinylidene chloride and a copolymerizable monomer.

[0015] As a vinylidene chloride and a copolymerizable monomer, methacrylic ester, such as acrylic ester, such as a vinyl chloride, a methyl acrylate, an ethyl acrylate, and butyl acrylate, a methyl methacrylate, ethyl methacrylate, and methacrylic-acid butyl, acrylic nitril, methacrylic nitril, etc. are mentioned, for example. Also among these, a vinyl chloride, acrylic ester, and methacrylic ester are often used industrially.

[0016] The larger one of the ratio of the vinylidene chloride in a vinylidene-chloride copolymer is desirable from a viewpoint of gas barrier nature, and it is 60 - 98 % of the weight more preferably 51 to 99% of the weight. Specifically in a vinylidene chloride / vinyl chloride copolymer, 80 - 95% of the weight of the range is desirable 70 to 95% of the weight at a vinylidene chloride / acrylic ester copolymer.

[0017] although especially the molecular weight of vinylidene-chloride system resin is not limited -- practically -- weight average molecular weight -- it is -- desirable -- 10,000-1 million -- it is 20,000-500,000 more preferably.

[0018] A vinylidene-chloride system resin layer may form the layer of further others on a vinylidene-chloride system resin layer, unless you may form on the surface of a battery case and the steam barrier nature of a vinylidene-chloride system resin layer and gas barrier nature are spoiled. When forming in a battery case front face, you may form in any of the front face of the side which touches a battery case inside front face, i.e., an electrolyte, and a battery case outside front face, and may form in the whole battery case front face, and may form in a part. As other layers further formed on a vinylidene-chloride system resin layer, fluororesin layers, such as PTFE, etc. are mentioned in order to give chemical resistance, for example.

[0019] Although determined by the engine performance which especially the thickness of a vinylidene-

chloride system resin layer is not limited, but is required of the formation approach of a vinylidene-chloride system resin layer, and a battery case, 0.5-200 micrometers is 1-100 micrometers more preferably practically.

[0020] Although the polypropylene resin which especially the quality of the material of the battery case body used for this invention is not limited, but is used from the former, ABS plastics, polyphenylene ether system resin, polystyrene system resin, etc. can be used. At the time of a moldability, rigidity, especially an elevated temperature (at the time of heat rigidity), oilproof and chemical resistance, warm water-proof permeability, The alloy resin of the polypropylene / polyphenylene ether system resin which uses the hydrogenation object of a dispersed phase and a styrene-butadiene copolymer as a compatibilizer for a matrix phase and polyphenylene ether system resin etc. can use polypropylene resin good from a viewpoint of cost.

[0021] Especially the formation approach of a vinylidene-chloride system resin layer is not limited, but is determined by the configuration of a battery case, the gas barrier engine performance demanded, processing cost, processing difficulty, etc. A vinylidene-chloride system resin film is specifically heated. A vacuum, The film laminated layers method which carries out lamination of the vinylidene-chloride system resin film to a battery case under the concomitant use conditions of a compressed air or a vacuum, and a compressed air, The spray painting method which carries out spray painting of the solution dip coating which is immersed in a battery case and forms a vinylidene-chloride system resin coat at a battery case into the solvent liquid which melted the vinylidene-chloride system resin emulsion solution which carried out the emulsion polymerization, and vinylidene-chloride system resin, an emulsion solution, and the solvent solution to a battery case is mentioned.

[0022] The vinylidene-chloride system resin complex film with which the surface consisted of a battery case and resin of the same kind as a vinylidene-chloride system resin film used for a film laminated layers method is desirable from an adhesive viewpoint. For example, in the battery case of a polypropylene resin, the complex film of the polypropylene resin and vinylidene-chloride system resin with which a surface consists of polypropylene resins of the same kind, "Bali Aron-CX#56" (the Asahi Chemical Industry Co., Ltd. make, trademark) etc., can use it good. [ for example, ] Although the monolayer film of vinylidene-chloride system resin, for example, a "saran film" (the Asahi Chemical Industry Co., Ltd. make, trademark) etc., can be used, in order to improve an adhesive property with a battery case, the approach of making a glue line placed between monolayer film or battery case sides, and carrying out a laminating is desirable.

[0023] The resin used for solution dip coating and a spray painting method has desirable vinylidene chloride / acrylic ester copolymer, and that whose ratio of acrylic ester is 5 - 20 % of the weight can use it good. When there is an inclination for film production nature to worsen [ the ratio of acrylic ester ] at less than 5 % of the weight and it exceeds 20 % of the weight, there is an inclination which becomes inadequate [ the gas barrier engine performance ]. The ratio of acrylic ester is determined from the balance of film production nature and the gas barrier engine performance. the molecular weight of a vinylidene chloride / acrylic ester copolymer -- weight average molecular weight -- 10,000-1 million -- the thing of 20,000-500,000 can use it good preferably.

[0024] As a solvent used for solvent liquid, what mixed a methyl ethyl ketone (MEK) and toluene can use it for a tetrahydrofuran good.

[0025] Also when forming a vinylidene-chloride system resin layer in a battery case by solution dip coating and the spray painting method, in order to raise an adhesive property according to the quality of the material of a battery case, it is desirable to perform priming beforehand.

[0026]

[Example] Hereafter, an example explains this invention concretely. This invention is not limited to the following examples.

[0027] In addition, extrusion molding (40mm full close bladed screw, ratio-of-length-to-diameter=27) of moisture vapor transmission and the gas transmittance was carried out on standard conditions (temperature suitable for sheet forming), they created the sheet with a thickness of about 0.4mm, and evaluated it based on the method of examining a degree.

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[0028] (1) Moisture vapor transmission : based on JIS-K7129B (the red sensor method), it measured on condition that 2 a transparency area of 50cm in 24 hours at the test temperature of 40\*\*5 degrees C, and 100% of relative humidity differences.

[0029] (2) Hydrogen gas permeability : based on JIS-K7126A (differential pressure method), it measured on condition that 2 a transparency area of 38.46cm in 24 hours by the test temperature of 40\*\*5 degrees C, and test-pressure 760mmHg.

[0030] (Example 1) 0.5 weight section addition of a zinc oxide / zinc sulfide =1/1 was carried out as a stabilizer at the charge of battery case material shown in Table 1, it kneaded at 280 degrees C of setup with the single screw extruder (the diameter full flighted screw of 40mm, ratio-of-length-to-diameter=27), and the twin screw extruder (ZSK-40, made in Woerner), the pellet was created, the sheet with a thickness of about 0.3mm was created by extrusion molding, and the sample of the magnitude of 300mm angle was obtained.

[0031] Subsequently, using the vinylidene-chloride system resin film shown in Table 1, with the vacuum forming machine, the vinylidene-chloride system resin film was heated at the temperature of 180 degrees C, and carried out the laminating on the surface of the sample. The measurement result of the moisture vapor transmission of the sample which carried out the laminating of the vinylidene-chloride system resin film, and gas permeability is shown in Table 2.

[0032] (Example 2) The sample of the magnitude of 150mm angle was obtained from the sheet used in the example 1. Subsequently, after immersing the sample and forming the coat of vinylidene-chloride system resin on the surface of a sample into the container into which the emulsion solution of the vinylidene-chloride system resin shown in Table 1 was put, it was left in the 60-degree C dryer for 2 hours. The measurement result of the moisture vapor transmission of the sample which covered vinylidene-chloride system resin (laminating), and gas permeability is shown in Table 2.

[0033] (Example 1 of a comparison) Moisture vapor transmission and gas permeability were measured in the condition as it is without carrying out the laminating of the vinylidene-chloride system resin for the sheet used in the example 1. A measurement result is shown in Table 2.

[0034]

[Table 1]

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重量部で配合

	実施例 1	実施例 2	比較例 1
電 槽 用 材 料	<p>ポリプロピレン／PPE樹脂／PS樹脂／水素添加スチレンーブタジエン共重合体＝60／25／15／10</p> <p>ポリプロピレン：旭化成ポリプロピレン E1100 (旭化成工業(株)製)</p> <p>PPE樹脂：クロロホルム中30℃での固有粘度が0.52であるポリ(2,6-ジメチル)エーテル (旭化成工業(株)製)</p> <p>PS樹脂：旭化成ポリスチレン 685 (旭化成工業(株)製)</p> <p>水素添加スチレンーブタジエン共重合体： タフテックH1081 (旭化成工業(株)製)</p>		
塩 化 ど ニ 系 リ 樹 脂 ン	<p>フィルム： バリアロン-CX #56 (旭化成 工業(株)製、商 標)</p>	<p>エマルジョン： 旭化成サランラテ ックス#536B (旭化成工業(株) 製、商標)</p>	なし
方 積 法 層	真空成形	浸漬	なし

[0035]  
[Table 2]

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	実施例 1	実施例 2	比較例 1
サンプルの全体厚み $\mu\text{m}$	445	396	386
塩化ビニリデン系樹脂層 の厚み $\mu\text{m}$	10	4~8 (両面)	なし
水蒸気透過率 $\text{g}/\text{m}^2 \cdot 24\text{hr}$	0.96	1.08	1.33
水素透過率 $\text{cm}^3/\text{m}^2 \cdot 24\text{hr} \cdot \text{atm}$	115	82	3035

[0036]

[Effect of the Invention] Since the battery case of this invention has a vinylidene-chloride system resin layer, it is excellent not only in steam barrier nature but gas barrier nature, such as hydrogen and oxygen.

[0037] Therefore, if it is in the sealing form rechargeable battery which uses the battery case concerning this invention, since it excels in steam barrier nature, disappearance of moisture is prevented and a rechargeable battery life is extended. Moreover, since it excels also in the gas barrier nature of activated gas, such as hydrogen and oxygen, not only maintenance of the cell engine performance but safety is secured.

[0038] This invention fills the severe engine performance required of a rechargeable battery, and responds to the miniaturization of a rechargeable battery, and advanced features.

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